CO HYDROGENATION OVER RHODIUM FOIL AND SINGLE CRYSTAL CATALYSTS: CORRELATIONS OF CATALYST ACTIVITY, SELECTIVITY, AND SURFACE COMPOSITION

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ABSTRACT

CO hydrogenation at 6 atm over polycrystalline Rh foil and single crystal Rh (111) catalysts was investigated in a system where the surface structure and composition of the catalysts could be characterized both before and after the reaction. The reaction conditions (H_2:CO ratio, reaction temperature, and surface pretreatment) were systematically varied to determine the optimum conditions for formation of oxygenated hydrocarbons. Initially clean Rh catalysts showed no structure sensitivity, primarily produced methane (90 wt%) at an initial rate of 0.15 molecules site^{-1}sec^{-1} at 300°C, and did not produce detectable amounts of oxygenated hydrocarbons. Preoxidation of the Rh catalysts (800 Torr O_2, 600°C, 30 min.) resulted in dramatically increased initial rates, a larger fraction of higher molecular weight hydrocarbons, some structure sensitivity, and formation of methanol, ethanol, and acetaldehyde. The different Arrhenius parameters over the clean and preoxidized foils indicate that the methanation mechanism is different on these two surfaces. Decreasing the reaction temperature or H_2:CO ratio increased the C_2H_4 to C_2H_6 ratio and shifted the product distribution towards higher molecular weight hydrocarbons.

INTRODUCTION

Reaction of H_2-CO mixtures over the Group VIII metals usually yields a wide range of products, including alkanes, alkenes, and oxygenated hydrocarbons. In recent studies,[1,2] Rh supported on SiO_2 showed a unique selectivity for production of the two-carbon oxygenated species acetaldehyde, acetic acid, and ethanol. Similar selectivity was shown at 1 atm on catalysts prepared by depositing Rh clusters on basic metal oxides.[3,4] This contrasts with results for Rh foil[5] and Rh supported on Al_2O_3,[6] over which no oxygenated hydrocarbons were formed at 1 atm. A need therefore exists for studying CO hydrocarbons over well-characterized Rh at elevated pressures, under a variety of reaction conditions and surface pretreatments, to determine the conditions necessary for oxygenated product selectivity. We have measured reaction rates and product distributions over clean and pre-oxidized Rh foil and Rh(111) crystal surfaces at 6 atm and 250-400°C, with H_2:CO ratios of 3:1 to 1:3. Surface structure and chemical composition were characterized using low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The results will be compared to previous results on Rh catalysts.

EXPERIMENTAL

The apparatus and technique employed in these experiments are described elsewhere.[5,7] Briefly, the reaction cell is located inside an ultra-high vacuum (UHV) chamber to allow ion sputter cleaning and surface characterization by LEED and AES immediately before and after reaction. After closing the cell, first the H_2 (99.9995% purity) and then the CO (99.99% purity,

Fe and Ni carbonyls removed in a dry ice trap) were admitted and circulated in the closed loop. Allowing a few minutes for mixing at room temperature, the reaction was then started by heating the Rh sample resistively. The buildup of products was monitored by a gas chromatograph using a Chromasorb 102 column and flame ionization detector. The reaction was stopped after times ranging up to 3 hr, by cooling to room temperature and pumping down to UHV, to measure changes in surface composition.

For preoxidized samples, the surface was heated to 600°C in 1 atm O_2 for 30 minutes inside the reaction cell. During this treatment, an epitaxial oxide was formed, and oxygen also dissolved into the bulk. The oxide layer was amorphous and had an O_{510}/Rh_{302} AES peak intensity ratio of 0.5 to 0.6, although ratios up to 2.6 were obtained by oxidizing carbon-covered surfaces.

The initial turnover numbers (TN) were determined from a least squares fit to the initial slope of the product concentration vs. time curves. In the calculation, the atom density of the Rh(111) surface (1.6×10^{15} atoms cm^{-2}) was used as the active site density. The same figure was also used for pre-oxidized samples, thus ignoring possible increases in surface area as well as a reduced Rh surface density on the oxide.

<div align="center">RESULTS</div>

Fig. 1 shows the buildup of products during a typical run on clean Rh at 300°C and $3H_2$:$1CO$. Results on the clean Rh foil and Rh(111) were identical. Under the above conditions, CH_4 was the main product (90 wt%) with initial TN 0.15 molecules $site^{-1}sec^{-1}$. C_2 and C_3 hydrocarbons were formed, but no oxygenated hydrocarbons were detected. All rates of product formation, ex-

cept C_2H_6, declined over the course of three hours. The AES spectra before
and after reaction, in Fig. 2, show that small amounts of S and Cl and a mono-
layer of C built up on the surface during CO hydrogenation. AES peak inten-
sities for these impurities remained nearly constant after the first 30 minute
minutes, although the reaction rates continued to decline. The proximity of
the Rh_{256} and Rh_{302} peaks prevented AES lineshape analysis to determine whe-
ther the carbon state was changing during this time.

Preoxidation of the Rh(111) crystal (see Figs. 3 and 4) greatly increased
the initial TN's, shifted product distribution slightly to higher molecular
weight, and resulted in the appearance of the oxygenated products methanol,
ethanol, and acetaldehyde. The marked decrease in TN's during the first 30
minutes coincided with rapid loss of the epitaxial oxide. After this period,
the near-surface oxygen concentration reached a low steady-state value, as
shown in Fig. 5. Methane was still formed at a higher rate on the steady-
state surface with oxygen than on the clean surface. Oxygenated products
were formed during the entire three hours. Decreasing the temperature led
to a further shift toward higher molecular weight and an increase in the C_2H_4
to C_2H_6 ratio, as shown in Figs. 6 and 7. During the CO-rich reactions acet-
aldehyde was the only oxygenated hydrocarbon produced. Also, two to four
monolayers of carbon were deposited on the preoxidized Rh during CO-rich runs
at $300^\circ C$, probably accounting for the increased poisoning rate (Fig. 6).

Results for preoxidized Rh foil were similar to those for preoxidized
Rh(111) except for a small structure sensitivity shown in a lower CH_4 TN and
larger C_2H_4 to C_2H_6 ratio. Also, ethanol formed a smaller fraction of the
oxygenated products. In CO-rich runs, more carbon was deposited on the pre-
oxidized foil than on preoxidized Rh(111), giving a faster poisoning rate.

The activation energy for methanation was found to be 12 kcal/mole on preoxidized foil, half the value (24 kcal/mole) found on clean Rh foil.[5]

DISCUSSION

Preoxidation of the Rh surfaces markedly changes their activity and selectivity, indicating that the chemical environment of the Rh atoms is important in determining their catalytic properties. This is consistent with the variability of supported Rh catalysts depending on their preparation.[1-4] The CH_4 formation rate depends directly on the oxygen concentration in the near-surface region, as shown in Table I. The lowest initial CH_4 production rate is obtained during CO hydrogenation over clean catalysts and the highest over the catalyststwith an epitaxial oxide. An intermediate value is given by peroxidized surface which are flashed in vacuum prior to CO hydrogenation,[5] resulting in a low near-surface oxygen concentration.[10] The fact that CO_2 hydrogenation gives a higher CH_4 TN than CO hydrogenation under the same reaction conditions suggests that CO_2 oxidizes the catalysts during hydrogenation. CO_2 has been shown to dissociatively adsorb on Rh surfaces,[8,9,11] and an oxygen AES signal was detected in the early stages of CO_2 hydrogenation over Fe.[12]

The changes in Arrhenius parameters, shown in Table II, strongly indicate that a change in mechanism is the cause of the increased CH_4 TN on preoxidized surfaces. In particular, a simple effect of surface area or active site density can be ruled out. The activation energy on the oxygen-treated surface is 12kcal/mole, half that on the clean surface, 24 kcal/mole,[5] and within experimental error of the value for CO_2 hydrogenation on clean Rh. This again

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suggests oxidation by the CO_2. Preexponential factors show a similar trend.

The effect of increasing pressure from 1 atm [5] to 6 atm (this study) was minor. The C_2H_4 to C_2H_6 ratio was smaller, presumably the result of the higher H_2 partial pressure increasing olefin hydrogenation. Also, the poisoning observed in this study at 6 atm was not observed at 1 atm. Possibly the effect of S and Cl impurities, or deactivation of C overlayers, is enhanced at high pressure. Behavior at 6 atm is in other respects similar to that at 1 atm [5] and agrees well with findings for supported Rh catalysts which produce hydrocarbons. [1,2,6] This indicates that metallic Rh or a complex of Rh and C is active in hydrocarbon formation, but that these surfaces do not provide the conditions necessary for oxygenated hydrocarbon formation, suggesting that a higher Rh oxidation state may be crucial to this process. Production of oxygenated hydrocarbons after the near-surface oxygen concentration reaches steady-state indicates that CO is the source of oxygen in these products, but bulk oxygen diffusing into the near-surface reagion is another possible source. We are undertaking isotopic labeling studies to resolve this question.

Varying the temperature and H_2:CO ratio produces results that follow the trends predicted for a mixture of products in equilibrium, [13] that is, higher molecular weight and more unsaturated or oxygenated products are favored at low temperature, and the hydrogen-poor species C_2H_4 and CH_3CHO are favored at low H_2:CO ratio. Thus thermodynamics seems to have relevance even though the overall CO-H_2 conversion to any of the products is far from equilibrium in our experiments. A possible explanation is that an initial slow step in the mechanism is followed by rapid combination and partial equilibration of hydrocarbon fragments.

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Table I. Comparison of initial methanation TN for CO and CO_2 hydrogenation in a batch reactor at $300^{\circ}C$ over Rh and Fe catalysts. Methane TN is in molecules site^{-1}sec.$^{-1}$

Catalyst	Reaction Conditions	Surface Pretreatment	Initial CH_4 TN at $300^{\circ}C$	Ref.
Rh foil	0.92 atm $3H_2$:1CO	clean preoxidized[a]	0.13 0.33	(5) (5)
Rh foil	0.92 atm $3H_2$:1CO_2	clean preoxidized[a]	0.33 1.7	(5) (5)
Rh foil	6 atm $3H_2$:1CO	clean preoxidized[b]	0.15 1.7	this study
Rh(111)	6 atm $3H_2$:1CO	clean preoxidized[b]	0.15 4.6	this study
Fe foil	6 atm $3H_2$:1CO	clean preoxidized[c]	1.9 18.7	(12) (12)
Fe foil	6 atm $3H_2$:1CO_2	clean	10.9	(12)

(a) 15 min at $300^{\circ}C$ in 700 Torr O_2, then heated to $1000^{\circ}C$ in vacuum.

(b) 30 min at $600^{\circ}C$ in 800 Torr O_2.

(c) 20 min at $300^{\circ}C$ in 4 atm O_2.

Table II. Comparison of the Arrhenius methanation parameters ($TN = A\,e^{-E_a/RT}$) for CO and CO_2 hydrogenation over polycrystalline Rh foils. Units for TN and A are molecules site^{-1}sec^{-1}. E_a is in kcal/mole.

Reaction Conditions	Surface Pretreatment	CH_4 TN at 300°C	A	E_a	Ref.
0.92 atm $3H_2$:1CO	clean	0.13 ± 0.03	10^8 [a]	24 ± 3	(5)
0.92 atm $3H_2$:$1CO_2$	clean	0.33 ± 0.05	10^5 [a]	16 ± 2	(5)
6 atm $3H_2$:$1CO_2$	preoxidized[b]	1.7 ± 0.4	10^5	12 ± 3	this study

(a) determined from data in Ref. (5).
(b) 30 min. at 600°C in 800 Torr O_2.

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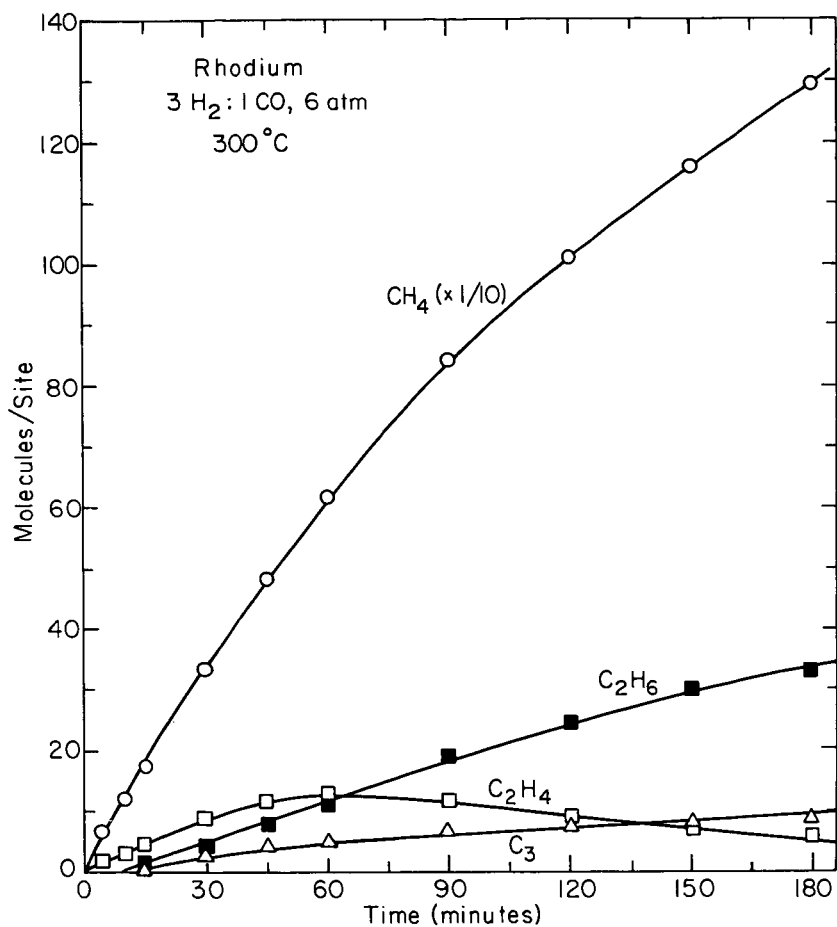
Fig. 1. Buildup of the C_1 to C_3 hydrocarbon products during CO hydrogenation over initially clean Rh foil or Rh(111) catalysts at 6 atm, 300°C, and $3H_2$:1CO.
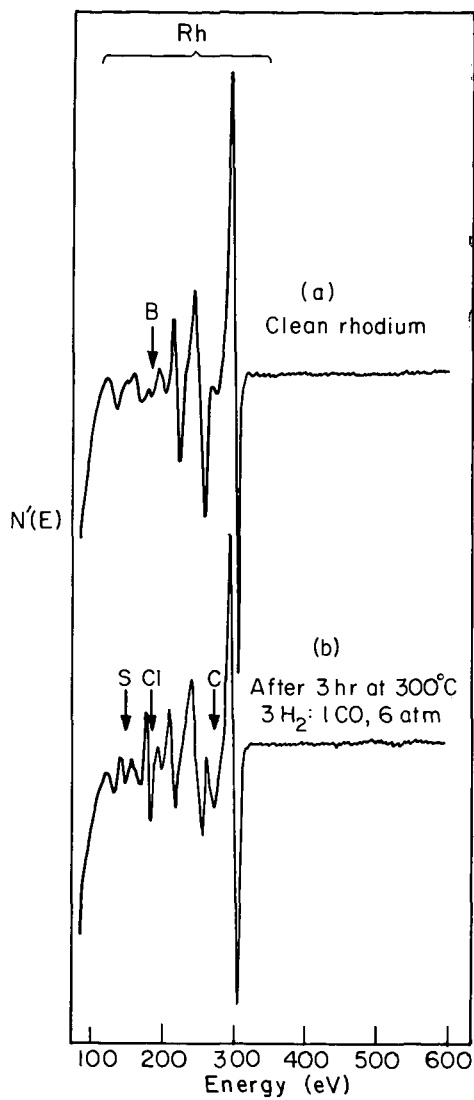
Fig. 2. AES spectra of the initially clean Rh catalysts (a) before and (b) after 3 hr of CO hydrogenation at 6 atm, $300^{\circ}C$, and $3H_2:1CO$.

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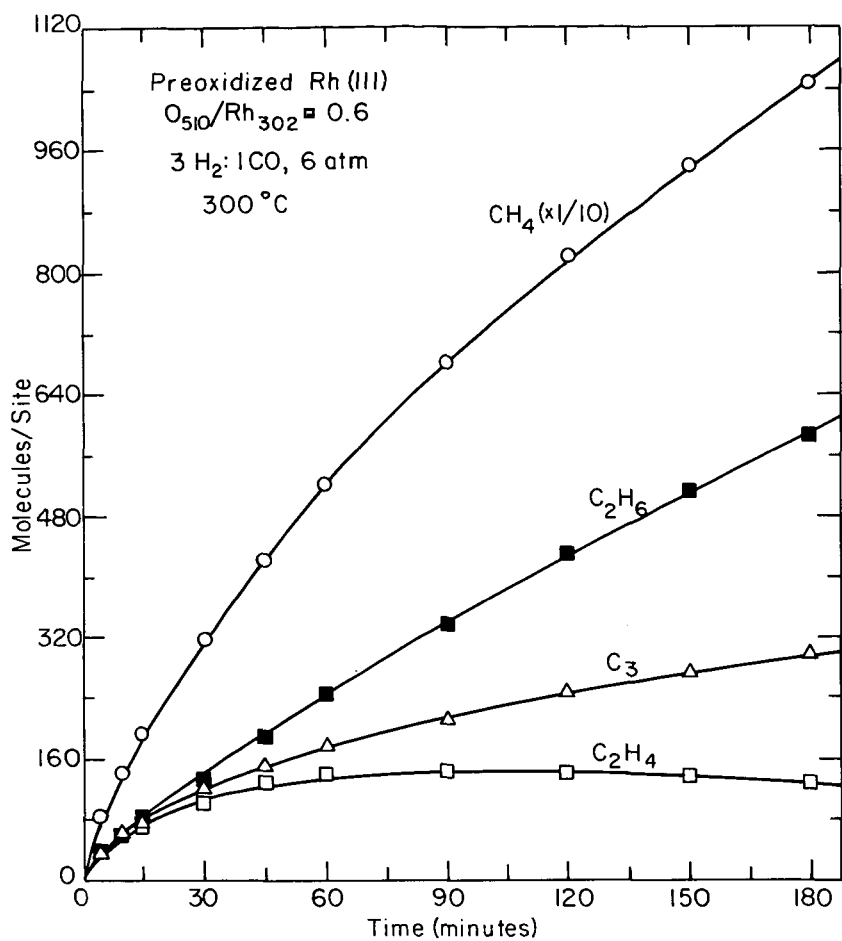
Fig. 3. Buildup of the C_1 to C_3 hydrocarbon products during CO hydrogenation over a preoxidized Rh(111) catalyst at 6 atm, 300°C, and $3H_2 : 1CO$.
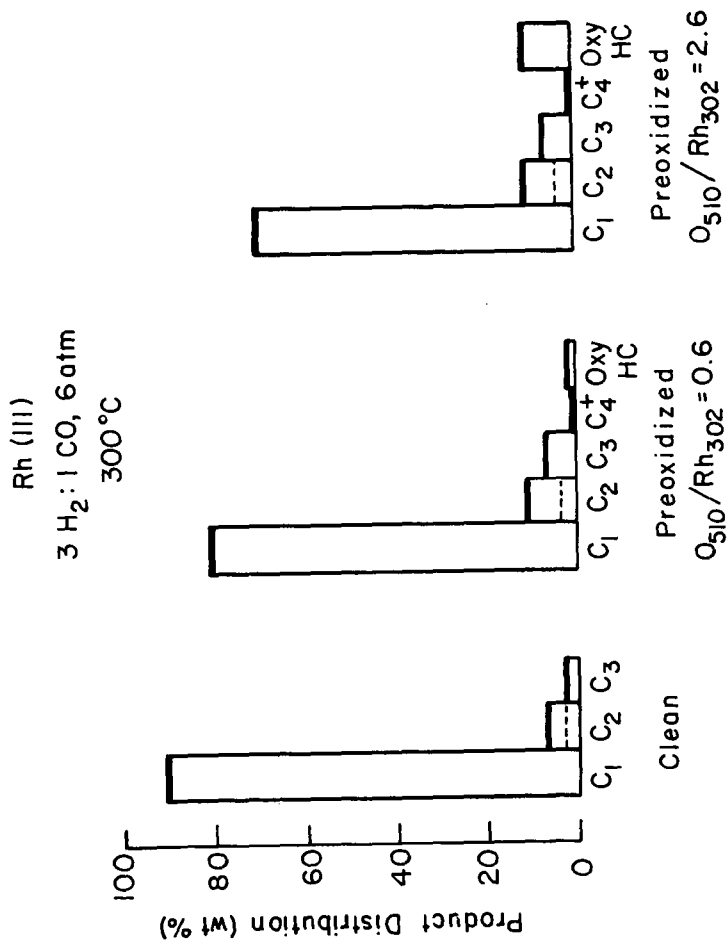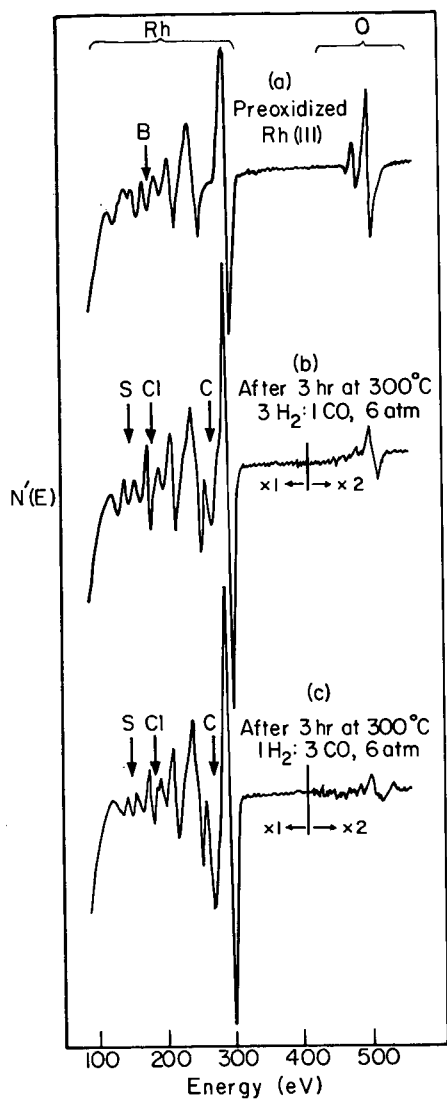
Fig. 4. The product distributions in weight percent after 2 hr of CO hydrogenation over pretreated Rh(111) catalysts at 6 atm, 300°C, and 3H$_2$:1CO. Oxy HC is the sum of the CH$_3$OH, CH$_3$CH$_2$OH, and CH$_3$CHO fractions. In the C$_2$ fraction the areas above and below the broken line represent the C$_2$H$_6$ and C$_2$H$_4$ fractions.

Fig. 5. AES spectra of the preoxidized Rh(111) catalyst (a) before and

(b) after 3 hr of CO hydrogenation at 6 atm, 300°C, 3H$_2$:1CO, or
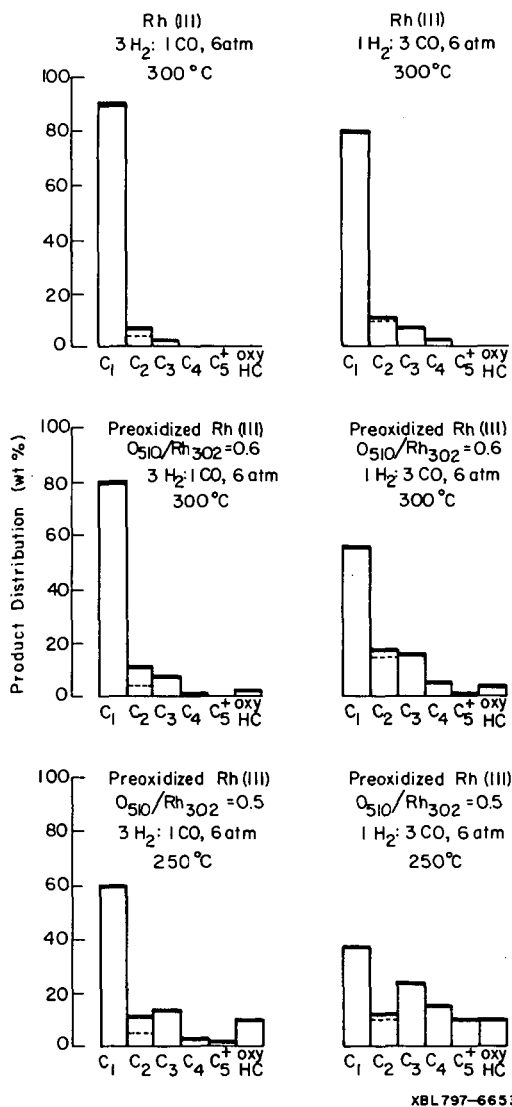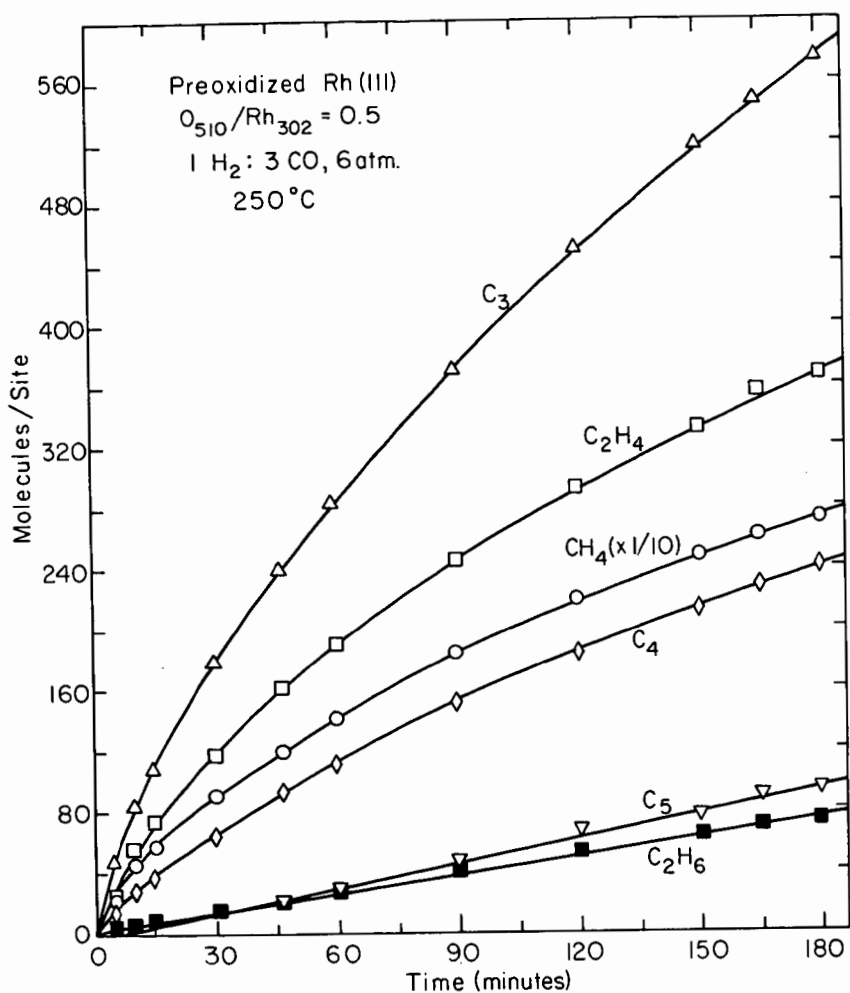
(c) after 3 hr of CO hydrogenation at 6 atm, 300°C, 1H$_2$:3CO.

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Fig. 6. Buildup of C_1 to C_4 hydrocarbon products during CO hydrogenation over a preoxidized Rh(111) catalyst at 6 atm, 250°C, and 1H_2:3CO.

Fig. 7. The product distributions in weight percent after 2 hr of CO hydro-
genation over pretreated Rh(111) catalysts at various reaction con-
ditions. See Fig. 4 for explanation of symbols.